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Magnetic specific heat of $CoCl_2$ and $FeCl_3$ intercalated in graphite

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We have studied the magnetic specific heat of first and second stages of both $FeCl_3$ and $CoCl_2$ intercalated in graphite. The behavior is very different on both sides of the transition: The broad high-temperature tails superimposable for both stages in both compounds indicates a two-dimensional (2D) behavior in this range of temperatures. For the first-stage compounds the low-temperature tail has a T^3 behavior, the maximum is stage dependent and is interpreted as a 2D to 3D crossover. We discuss the shape and the origin of these magnetic specific heats according to 2D models which should include in these compounds the islandic nature of the intercalated layers.

I. INTRODUCTION

The magnetism of graphite intercalation compounds (GIC) with metal chlorides is a very rich field, especially because they are among the best of magnetic systems which approach two-dimensional (2D) model behavior. This is due to the possibility of changing the distance between two nearest magnetic layers by a varying of the stage of the compound (the number of carbon planes which separate two adjacent intercalated layers). Unfortunately, an important effect strongly modifies this ideal behavior: The intercalated layer is not continuous, and is better described as a number of in-plane islands.[1] This seems to be an intrinsic effect due to the large contraction which occurs in the layer between preparation and room temperatures. The 2D theories were elaborated for infinite systems and it was recently shown in magnetic susceptibility measurements that the dipole-dipole interaction between the "supermoments" of the islands are responsible for the observed peak.[2] We have recently applied this idea with success to second-stage $CoCl_2$ GIC and shown that there exists a crossover temperature between a high-temperature infinite 2D-system behavior and a low-temperature regime which is driven by the in-plane size of the islands.[3] We have also shown that the values of the critical exponent γ vary with the c-axis repeat distance, which indicates a deviation from an ideal 2D system. We have attributed this effect also to the dipole-dipole interaction along the c axis. Some specific-heat measurements have already been performed in these systems. For $CoCl_2$ GIC (Refs. 4 and 5) or mixed $CoCl_2$-$AlCl_3$ GIC,[6] the magnetic contribution consists of a weak and broad maximum at around 8 K. The results were interpreted as those of a 2D XY system, according to the nature of pristine $CoCl_2$ which is an XY system.[7] In $FeCl_3$ GIC's, Onn *et al.*[8] have found a similar behavior, with a maximum at 1.9 and 3.8 K in the first and second stage, respectively, though pristine $FeCl_3$ is known as a Heisenberg system.

In this paper, we present new results obtained on well-characterized powdered samples of the first and second stage of both $FeCl_3$ and $CoCl_2$ compounds.[9,10] After a description of the samples and their structure in Sec. II, we present in Sec. III the specific-heat results, which are discussed in Sec. IV.

II. SAMPLES

The samples that we have used were prepared from powdered graphite. A mixture of the metal chloride ($CoCl_2$ or $FeCl_3$) and of graphite was heated for several weaks under chlorine-gas pressure. The temperature was fixed at the value necessary for obtaining a GIC with the desired stage.[11] The stage of the intercalation was checked by x-ray diffraction.

The crystalline structures of these GIC's are incommensurate: Graphite and intercalate layers keep their own structure with little modification. Graphite is a honeycomb lattice ($a=b=2.455$ Å, $\gamma=120°$). $X Cl_2$ ($X=$Co or $Fe_{2/3}$) is made of two triangular chlorine lattices with X in the corresponding octahedral sites. In $CoCl_2$, every site is occupied. The Co^{2+} lattice is hence triangular ($a=b=3.54$ Å, $\gamma=120°$). In $FeCl_3$, one of every three sites is left empty, which gives a honeycomb lattice ($a=b=6.12$ Å, $\gamma=120°$). In Fig. 1 these lattices are summarized. Graphite and chlorine lattices are incommensurate $3.54/2.445=1.44$, but their unit vectors are parallel. The stacking of the layers depends on the stage of the intercalation. In the first-stage compound, the stacking is AAA for both graphite and $X Cl_2$ with 30% of stacking faults.[12] In the second-stage compound, the stacking is completely random and the compound can be considered as a 2D system.

We have used three different methods to determine the size of the islands in our samples. The chemical composition was checked by chemical analysis and we have found the formulas given in Table I. From these formulas, we

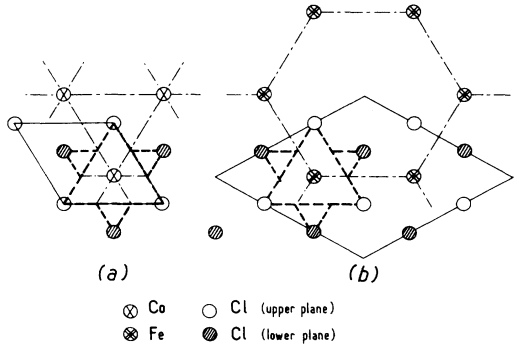

FIG. 1. In-plane structure of the metal chlorides layers. (a) $FeCl_3$; (b) $CoCl_2$. The unit cell is presented in dot-dashed lines, the metallic lattice is also represented. One of the octahedral sites is presented in each case.

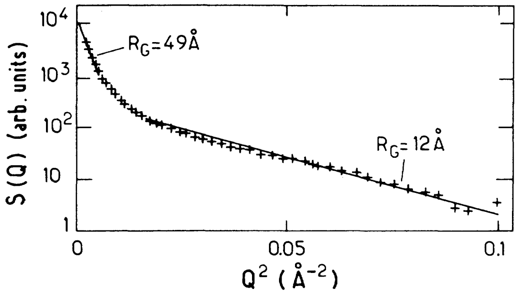

FIG. 2. Guinier plot [$\ln S(Q)$ vs Q^2] of the $CoCl_2$ GIC, with two regimes which indicate two characteristic gyration radii 12 and 49 Å.

can obtain the coverage ratio in chlorine by a comparison to the stoichiometric formula $C_{4.16s}XCl_2$ (s is the stage). The value of 4.16 is obtained by the ratio of the unit cells. The actual chemical composition is $CoCl_{2(1+x)}$. If one assumes that the supplementary chlorine atoms are on the edge of the island[1] (on only one side in fact), the diameter of the islands is $2R=2a/x$. For a circular island $2R=120$ Å (i.e., 275 atoms) for $x=0.12$ and $a=3.54$ Å. The width of $(h\,k\,0)$ peaks in neutron diffraction gives a similar value for the in-plane coherence length. We have also performed small angle neutron scattering on the D17 diffractometer of the Institut Laue Langevin (Grenoble, France) and found similar results as the Guinier plot ($\log_{10}[S(Q)]$ versus Q^2) of Fig. 2 shows. In this figure, one can observe two different radii: the 50-Å radius is the in-plane radius and the 12-Å radius, the c-axis coherence length which is close to the repeat distance of the compound (12.7 Å).

In $CoCl_2$ GIC, the charge transfer is due to the composition

$$Co^{2+}+2(1+x)Cl^- ,$$

which induces a charge transfer to the graphite of xe^- per Co atom. In $FeCl_3$ GIC, the corresponding formula is different because of the existence of two different ions:

$$(1-x')Fe^{3+}+x'Fe^{2+}+3Cl^- ,$$

which introduces a charge transfer of $x'e^-$ per Fe atom. After reaction with the water of the atmosphere, a certain amount of chlorine goes out of the sample; this gives

TABLE I. Various characteristics of the four samples that we have studied.

	Compound			
	$CoCl_2$ GIC		$FeCl_3$ GIC	
Stage	1	2	1	2
Chemical formula	$C_{5.23}CoCl_{2.12}$	$C_{10.3}CoCl_{2.12}$	$C_{7.87}FeCl_{3.17}$	$C_{12.95}FeCl_{2.85}$
Coverage (%)	84	85	84	91
Magnetic susceptibility				
Temperature of the maximum (K)	7.5	8	5.5	no maxium
Temperature of the crossover (K)		9.2	6.9	
Neutron scattering:				
critical temperature (K)	10		5.5	no transition
Specific heat				
A ($J\,g^{-1}K^{-1-b}$)	2.57×10^{-4}	1.2×10^{-4}	2.82×10^{-4}	4.17×10^{-4}
b	1.5	1.8	1.57	1.4
Entropy recovered at low temperature (k_B/atom)	0.31 (at 6 K)	0.45 (at 3.1 K)	0.74 (at 3 K)	0.74 (at 2.2 K)
Entropy recovered above T_m (k_B/atom)	0.21	0.30	0.56	0.57
T_m (K)	9.7	7.8	3.7	4.2
Temperature of crossover (K)	10.2	10.3	7.3	7.3

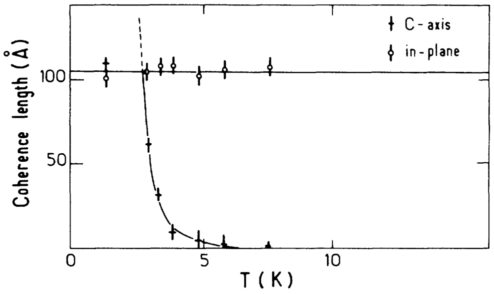

FIG. 3. In-plane and out-of-plane correlation lengths vs temperature in the first-stage $FeCl_3$ GIC.

$$(1-x')Fe^{3+}+3(1-x')Cl^{-}+x'Fe^{2+}$$
$$=(1-x')[Fe^{3+}+x'/(1-x')Fe^{2+}+3Cl^{-}]\ .$$

This transformation is associated to a change of the structure since the Fe^{2+} occupy the empty sites of the honeycomb lattice. In $FeCl_3$ GIC's, two kinds of compounds exist.[13] The main difference is the value of the crystalline parameter "a" which is 6.12 or 6.06 Å. According to the chemical formula and to x-ray results of Table I, the samples that we have studied are of the second type.

We have performed on the same samples magnetic susceptibility measurements and neutron scattering. In $CoCl_2$ GIC's, the magnetic susceptibility presents a broad maximum interpreted by the "superferromagnetic" model, and a crossover to an "infinite system" behavior above $1.24T_c$.[3] Neutron scattering experiments have shown in $CoCl_2$ GIC's a c-axis antiferromagnetism in both first-[10] and second-stage compounds.[13] It was not possible to observe any in-plane structure and a ferromagnetic interaction is assumed.

In $FeCl_3$ GIC's, the magnetic structure is more complicated: the in-plane structure is an incommensurate in-plane modulation. We have observed in the first-stage compound and not in the second one a 2D-to-3D crossover at about 5 K. Figure 3 presents the behavior of both in-plane and out-of-plane correlation lengths in the first-stage compound as determined from the width of the magnetic neutron diffraction experiment already published.[14] The magnetic susceptibility presents a maximum at 5.5 K and its second-derivative singularities at 5.5 K and 6 K.[10] Table I summarizes all these experimental temperatures.

III. SPECIFIC-HEAT RESULTS

The specific-heat measurements were performed by a dynamical adiabatic differential method, as previously described.[15] The samples were sealed in copper containers in the presence of a mixture of helium and nitrogen gas to realize the thermal coupling with the container without any extra adsorption peak in our experimental range of temperature. An empty container was used as a reference.

Figure 4 presents the experimental results of the specific heat of the first and second stage of $CoCl_2$ and $FeCl_3$ GIC's. These results are also compared to some previous ones[6,8] on the same figure. In addition to the lattice contribution, a clear magnetic contribution appears. This magnetic part presents always a maximum and a broad high-temperature tail. The result of Shayegan *et al.* was obtained with a $AlCl_3$-$CoCl_2$ mixed GIC in which there is only 20% of $CoCl_2$ per layer. As one can see in Fig. 4, the magnetic contribution is much smaller than in our case. The result of Onn *et al.* for the first-stage $FeCl_3$ GIC is very similar to our result, but the second-stage compound gives completely different results. There is no simple explanation since Onn *et al.* do not tell which kind of $FeCl_3$ GIC they have used.

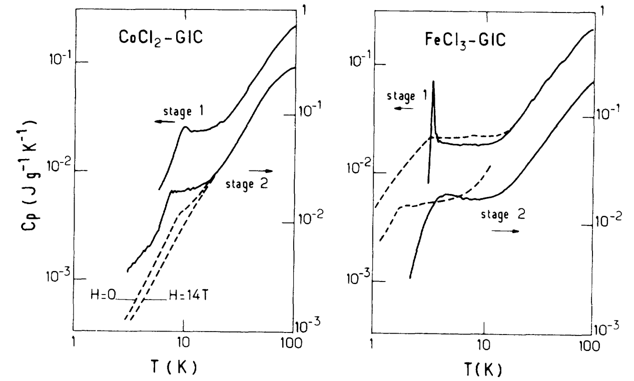

FIG. 4. Experimental results for the specific heat in both first and second stage of $FeCl_3$ and $CoCl_2$ GIC's. Dashed lines represent the experimental results of Shayegan *et al.* (Ref. 6) for $CoCl_2$ GIC and Onn *et al.* (Ref. 8) for $FeCl_3$ GIC.

In the first-stage compounds, there exists also a very narrow peak which is not reproducible as shown in Fig. 5: this peak occurs over a very wide range of temperature. Since this peak does not exist in the second-stage compounds, it is not possible to explain it by a spurious effect. The application of 5 T makes it disappear definitively, even after an annealing at room temperature. This is a very strange effect that we attribute to an irreversible field-induced structural phase transition, but which

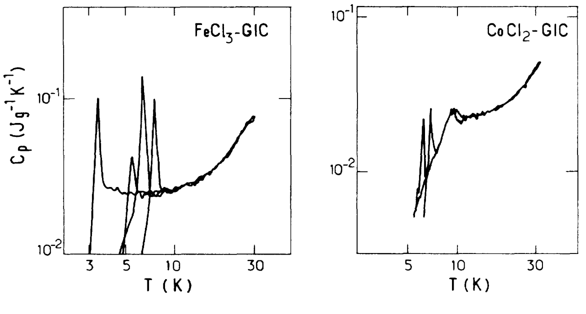

FIG. 5. Specific heat of the first-stage compounds. This curve presents the nonreproducibility of the narrow peak in the first-stage compounds.

should be discussed with more details later.

In order to study the magnetic part, it is necessary to subtract the nonmagnetic part of the specific heat. Because of the lack of any detailed investigations of the lattice dynamics in metal chloride intercalation compounds, we have chosen an empiric method: since the curvature of the nonmagnetic specific heat of any graphite intercalation compound is always negative in a double-logarithmic scale,[6] and since this is also true in the mixed $CoCl_2$-$AlCl_3$ samples in presence of a strong magnetic field,[6] we have chosen the low temperature part of the nonmagnetic specific heat equal to a straight line obtained by continuity at the inflexion point of the observed curve. This nonmagnetic part is very close to the result presented in Fig. 4 with an applied field for one of the compounds. This method is good near the inflection point, since we do not wait for a large change in the nonmagnetic slope, and it is also good at low temperature, since the nonmagnetic part is much smaller than the magnetic one. In the intermediate range, the error due to an error on the slope of the nonmagnetic part should not be greater than 5%. Table I gives the parameters A and b for the four samples and pristine graphite ($C_p - AT^b$)

Figure 6 presents the magnetic parts that we have obtained by this data treatment, normalized per magnetic atom, according to the actual chemical compositions. The four curves are very similar, except for the narrow peaks of the first-stage compounds. The two curves of the same compound are nearly superimposable in the high temperature side, above the maximum, which indicates the absence of any magnetic coupling along the c direction. In every curve, a large anisotropy exists between the two sides of the transition.

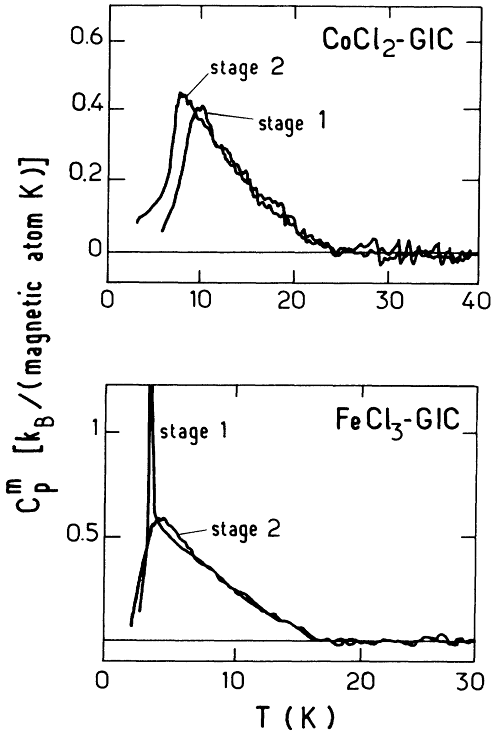

FIG. 6. Magnetic part of the specific heat as a function of temperature.

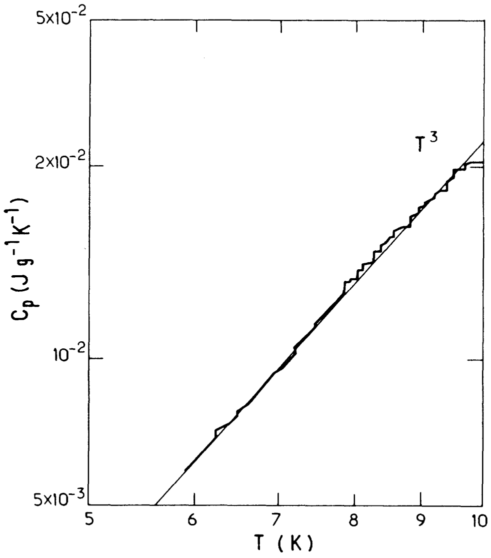

FIG. 7. Low-temperature part of the specific heat of the first-stage $CoCl_2$ GIC as a function of temperature showing the T^3 behavior.

The behavior of the low-temperature part is difficult to analyze in the first-stage compounds, because of the presence of the narrow peak. However, in the part which is common to every curve, a T^3 behavior was found, which can be due to 3D magnons (Fig. 7), since there is a 3D coupling in this range of temperature.

By using the formula

$$S = \int_{T_{\max}}^{T_{\min}} \frac{C_p^m(T)}{T} dT ,$$

we have calculated the entropies recovered at a given temperature. A large amount of the entropy is recovered at the lowest temperature, but the curve does not completely saturate. The entropy which corresponds to the narrow peak is in the first stage compounds, on the contrary, very small. The entropy recovered in the high-temperature tail corresponds to the ordering of the spins inside an island. At lower temperatures, the ordering concerns the interisland interactions. Table I gives the numerical values of the entropies recovered at the maximum of the specific heat and at the lowest reached temperature.

IV. DISCUSSION

The magnetic specific heat is very asymmetric in all the samples: the low-temperature part (below the maximum) is stage dependent while the high-temperature part does not depend on the stage. For this reason, we assume that the high-temperature tail corresponds to an in-layer behavior. In $FeCl_3$ GIC's, we have observed by neutron scattering in the first-stage compound that the transition corresponds to the 3D-to-2D crossover, as it is seen on the magnetic coherence lengths on Fig. 3: The maxima of specific heat and susceptibility occur at the temperature where the out-of-plane coherence length becomes infinite. In the second-stage compound, we did not observe such a crossover and the compound remains 2D in the whole temperature range. In $CoCl_2$ GIC's, we have observed at low temperature a *c*-axis antiferromagnetism in both first-[10] and second-stage [13] compounds. This is consistent with the T^3 law in our specific heat (Fig. 7). We did not observe any 2D fluctuations above T_c by neutron scattering in our samples. As this is difficult to observe in powdered samples, we have repeated the experiment with a highly oriented pyrolytic graphite first-stage compound[10] and we did not observe any 2D fluctuations in this case either. On the contrary, others[16] have observed a 2D ridge along the *c* axis in a second-stage sample of Kish crystals.

In all the samples, we understand the order at high temperatures as an in-cluster order and hence as short-range 2D fluctuations. These results are different from those of magnetic susceptibility in $CoCl_2$ GIC (Ref. 3) which shows for the high-temperature part a law $(T-T_c)^{-\gamma}$ where the exponent corresponds to a 3D law. They were interpreted as resulting from the influence of finite-size effects and the dipole-dipole interactions along the *c* axis. But a $(T-T_c)^{-\gamma}$ law with very large γ values is much more sensitive to a 3D coupling than a $(T-T_c)^{-\alpha}$ law with α close to zero. However the plot on a double-logarithmic scale of the specific heat results (Fig. 8) also shows a crossover between a $(T-T_c)^{-\alpha}$ law and the saturation regime. This crossover is not as clear as in the susceptibility but it can be interpreted by the same kind of effect: the limited size of the in-plane islands. The maxima of the magnetic specific heat and susceptibility are not at the same temperature: they differ by about 2 K. This difference is not well understood. It can be due either to a dipole-dipole coupling effect which should affect differently the two properties or to the *XY* nature of the system. Such a behavior is indeed predicted in the Kosterlitz-Thouless transition in which the specific heat presents only an essential singularity at the transition,[17] far below the maximum of the specific heat itself. As there is no universal behavior in the magnetic specific heat of a 2D *XY* system,[17] numerical simulations on these systems are now in progress in order to confirm all these ideas.

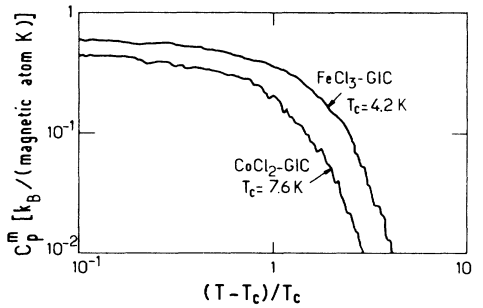

FIG. 8. Magnetic contributions of the specific heat as a function of reduced temperature in a double logarithmic scale for the second-stage compounds.

The most intriguing fact is the similarity of the $FeCl_3$ GIC and $CoCl_2$ GIC behavior in Fig. 6, though they are currently known as Heisenberg and *XY* systems, respectively. This confirms once more that the in-plane size of the islands and the dipole-dipole coupling are probably more important than the specific behavior of a given model (there is no transition in a Heisenberg model and an essential singularity in an *XY* model).

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